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Optical activity in the isotropic and blue phases of two cholesterics

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Optical activity measurements were performed in the isotropic phase and blue phases of two short-pitch cholesteric liquid crystals (cholesteryl oleate and cholesteryl oleyl carbonate). The data in the isotropic phase are interpreted in terms of five structural modes of the order parameter. Coupling between these modes gives rise to an extremum and a change of sign in the pretransitional optical rotation. The intensities of the polarized and depolarized component of the transmitted beam were measured as an extra tool to locate the phase transitions.

1. Introduction

Recently significant progress has been made in the understanding of how order is built up in a fluid going from the isotropic to the chiral nematic phase. Cholesterics with high chirality are especially intriguing because of the appearance of the so-called blue phases [1]. In the isotropic phase some kind of short range order increases on approaching the phase transition. According to the Landau-de Gennes theory [2], confirmed by experiment, this local anisotropy results in a sharp increase in a number of properties, e.g. the electric- or magnetic-induced birefringence and the intensity of scattered light. Cheng and Meyer [3] showed that an enhancement of the optical rotation can also be observed in the isotropic fluid as a result of pretransitional short range chiral ordering. Dolganov *et al.* [4] confirmed experimentally the divergent behaviour in a mixture of 4-methoxy-benzylidene-4-*n*-butylaniline and a cholesteryl capriate. They were able to explain their data with a model based on a Landau-de Gennes expansion. Bensimon *et al.* [5] confirmed later the Dolganov results, but they enlarged the scope by treating also the blue phases.

All of these studies considered only one fluctuation mode and obtained, quite normally divergencies of the form $(T - T^*)^{-1/2}$. Filev [6] drew attention to the fact that fluctuation modes that do not cause optical rotation ϕ directly may become active by mode coupling. He predicted a competition of two divergent contributions with opposite sign giving rise to an extremum in $\phi(T)$. Demikhov and Dolganov [7] claimed experimental confirmation of the maximum for cholesteryl nonanoate: the distance between the extremum and the transition temperature was extremely small and these results could not be confirmed [8]. Some evidence of a maximum has also been given by Beevers *et al.* [9]. More recently, Battle *et al.* [8] carried out a convincing experiment in the system CE2 with a chirality at least twice as great as that of cholesteryl nonanoate. In order to provide more evidence and to make detailed comparisons with theory, we have carried out measurements of the optical rotation in two cholesteryl esters: they both show the extremum in ϕ and confirm the effect of mode coupling proposed by Filev [6].

2. Theoretical background

When a linearly polarized wave travels in the z direction through a fluid over 1 cm the plane of polarization will rotate through an angle $\phi_{\text{tot}} = \phi_0 + \phi$. Here ϕ_0 is the molecular optical rotation, given by

$$\phi_0 = \frac{16\pi^3 N}{\lambda^2 C} \beta, \quad (1)$$

where β is the optical rotatory parameter, which is a molecular property, and N is the particle density [10]. This expression is valid if the fluid is orientationally disordered. The structural optical rotation ϕ appears as soon as orientational correlations exist, even if the correlation length is very small. This second effect has been treated by several authors [3–6]. The conditions can be summarized as follows [5, 6]:

- (a) Five independent structural modes exist (m , being the label of the mode, may be ± 2 , ± 1 , 0 for, respectively, the planar spiral, the conical spiral and the non-chiral mode).
- (b) Each mode has its own correlation length and a characteristic temperature T_m^* where it diverges. All T_m^* are lower than the transition temperature and $T_1^* < T_2^*$.
- (c) If no coupling exists between the modes, only the $m = +1$ mode matters and the optical rotation will diverge at T_1^* with a power law $(T - T_1^*)^{-1/2}$ according to

$$\phi_{\text{tot}} = \phi_0 + A \frac{T}{(T - T_1^*)^{1/2}}, \quad (2)$$

in which

$$A = \frac{kk_0^2 q_0}{48\pi\bar{\epsilon}(a_0 b)^{1/2}} \left(1 + \frac{c}{2b}\right)^{-3/2}.$$

- (d) If higher than second order terms in the Landau expansion are allowed, cross terms between $m = 1$ and $m = 2$ occur, giving rise to an additional optical rotation. In spite of being a higher order effect, it may be quite large because the $m = 2$ fluctuation diverges at $T_2^* (> T_1^*)$. Filev [6] showed that the coupling effect has the opposite sign of the $m = 1$ contribution and that the total optical activity in the isotropic fluid close to the chiral nematic phase transition is given by

$$\phi = \phi_0 + AT \left(\frac{1}{(T - T_1^*)^{1/2}} - \frac{f(x, T - T_2^*)(1 + c/2b)^{3/2}}{(T - T_2^*)^{1/2}} \right), \quad (3)$$

with $x = \lambda/P$ (P is the pitch). The function f is rather strongly dependent on temperature for $x = 1$ [6].

3. Experimental

The samples used in our experiments were cholesteryl oleate (CO) and cholesteryl oleyl carbonate (COC). Both were obtained from Van Schuppen (The Netherlands) and used without further purification. The samples were contained in a glass cell (1 cm path length), located in a triple oven arrangement and installed in a temperature controlled room. The temperature stability of the shield surrounding the cell could be kept at better than ± 1 mK for periods of days. The optical activity was measured

using a modified automated polarimeter type AA10 made by Optical Activity, Great Britain. The light source consisted of an interference line filter that transmitted the 5890 Å line of a tungsten lamp. The beam passing the sample and the analyser rotating at 7 Hz, was finally detected by a silicon photodiode. The phase difference between the analyzer motor driver signal and the photodiode output was measured by a phase difference detector, giving the average optical rotation angle with a precision of about $\pm 0.01^\circ$. The periodic maxima of the photodiode output gave a measure of the transmitted polarized component, and the minima were related to the depolarized component. Both values have been recorded.

Measurements of the optical activity and the transmitted intensities were taken as a function of the temperature, starting in the cholesteric phase (no transmission). Preset ΔT jumps were made under computer control: readings were only taken when the value of ϕ has been constant for some time, so that apparently equilibrium has been reached.

4. Results

Data for the rotation angle ϕ and for the intensity are given for CO in figure 1 and for COC in figure 2. From our data the transition temperatures were identified as shown in table 1. The cholesteric–BPI phase transition is identified by a sudden increase of the transmitted intensities. The BPI–BPII transition is identified by a jump in the optical activity and in the transmitted intensities. There is no clear evidence of a BPII–BP III transition, but there is some indication for a jump in the transmitted intensity (see, for example, COC). The transition temperature to the

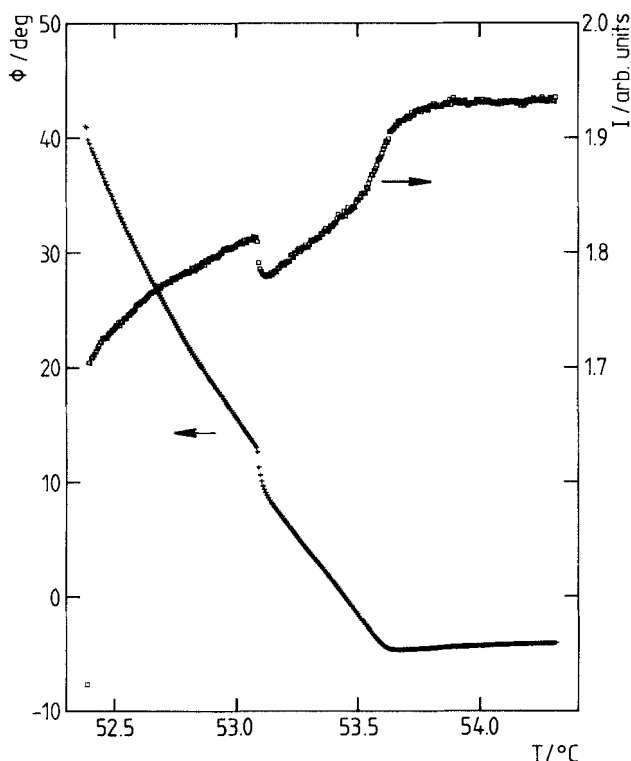


Figure 1. Transmitted intensity (\square) and optical rotation ($+$) for cholesteryl oleate.

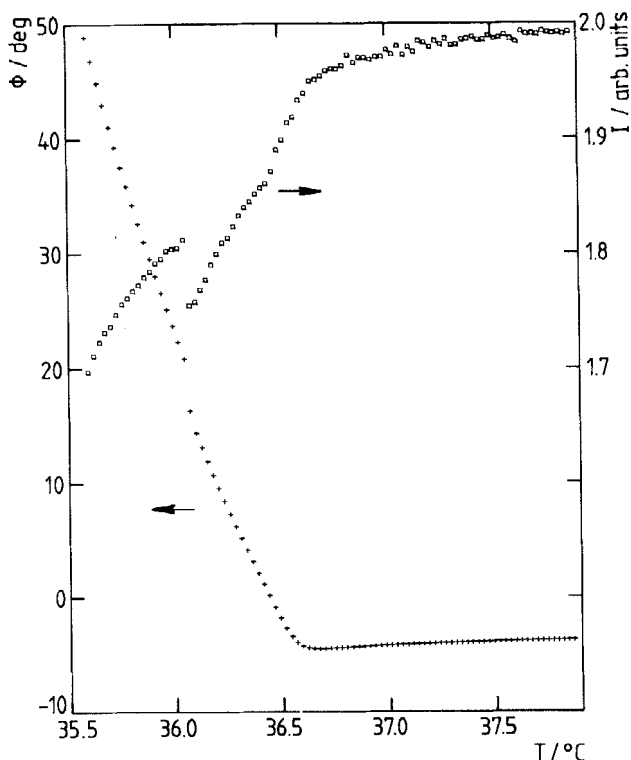


Figure 2. Transmitted intensity (\square) and optical rotation ($+$) of cholesteryl oleyl carbonate.

Table 1. Transition temperatures of CO and COC ($T/^{\circ}\text{C}$)

	Ch	BPI	BPII	BP III	I
CO	52.35	53.09			53.57
COC	35.55	36.06	(36.29)		36.47

isotropic fluid is located by a discontinuity in the slope of the $\phi(T)$ and $I(T)$ curves. However, in contrast with Demikhov's result for cholesteryl nonoate, we did not observe an appreciable jump in ϕ itself.

5. Analysis of the data

It is immediately clear from figures 1 and 2 that the data give at least a qualitative confirmation of the Filev prediction, including the extremum in ϕ and the change of sign. Far from the phase transition the correlation lengths of the fluctuation modes are small compared with λ and the fluctuation part of the rotation of the polarization is determined by the conical spiral mode [6]. This can be checked by plotting $(\phi - \phi_0)^{-2}$ as a function of temperature. If equation (2) is applicable, this graph should be a straight line [4, 7]. Figures 3 and 4 confirm that this is the case for CO and for COC down to about 0.5 K above the transition temperature. The most probable values of the fitting parameters are given in table 2.

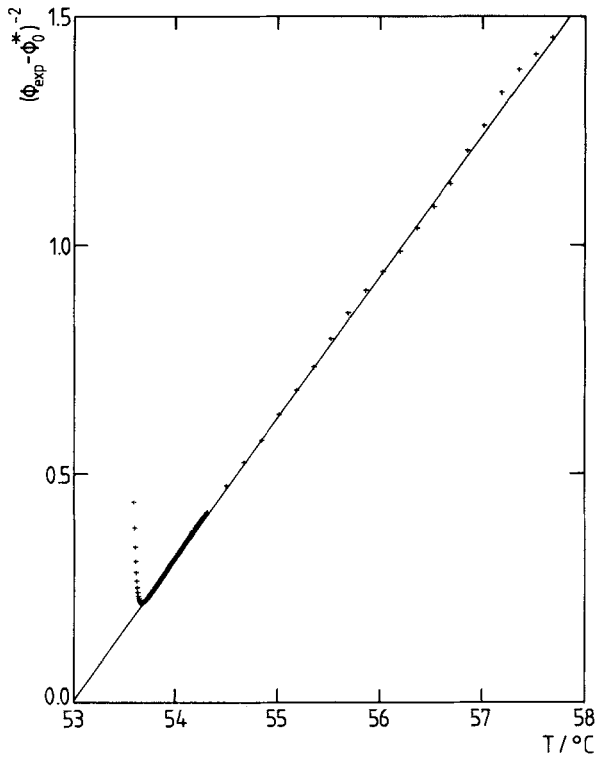


Figure 3. $(\phi_{\text{exp}} - \phi_0^*)^{-2}$ versus temperature for cholesteryl oleate.

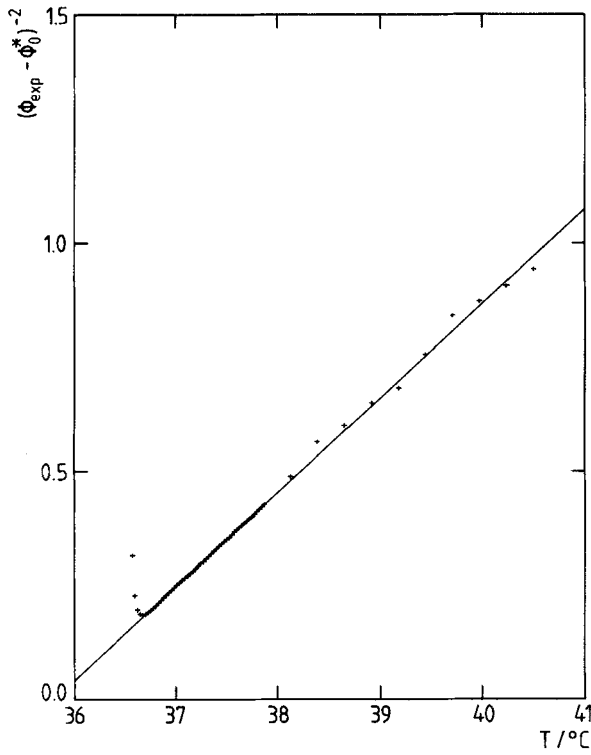


Figure 4. $(\phi_{\text{exp}} - \phi_0^*)$ versus temperature for cholesteryl oleyl carbonate.

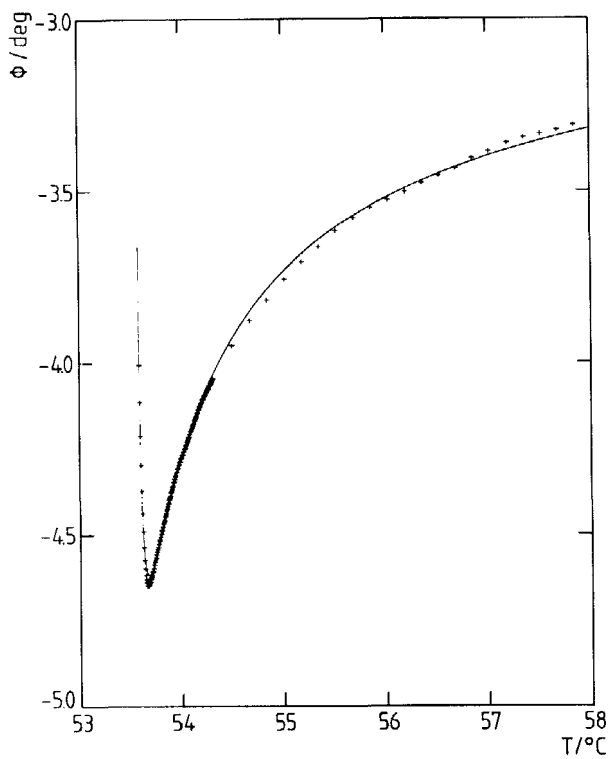


Figure 5. Optical rotation for cholesteryl oleate: experiment (+) and theory (—).

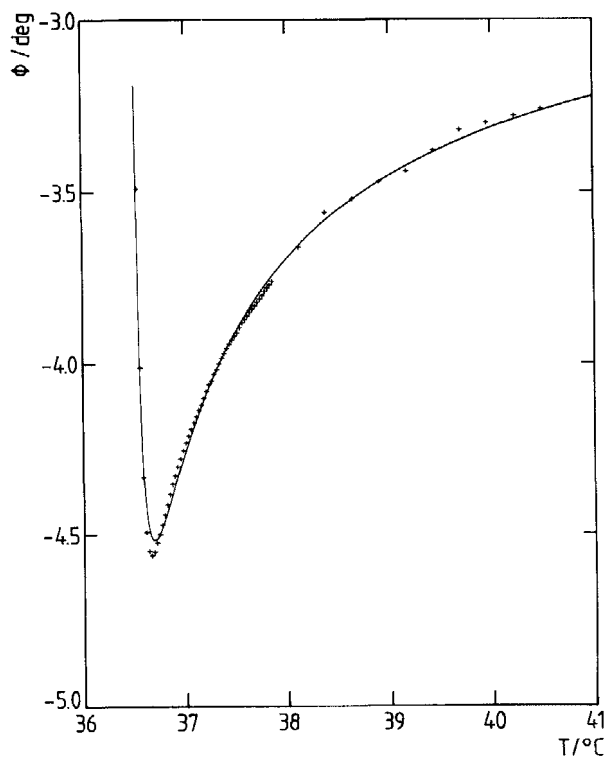


Figure 6. Optical rotation for cholesteryl oleyl carbonate: experiment (+) and theory (—).

Table 2. Parameters required to linearize $(\phi_{\text{exp}} - \phi_0^*)^{-2}$ versus temperature.

	ϕ_0^*/deg	$T_1^*/^\circ\text{C}$	Slope/ $\text{cm}^2 \text{K}^{-1} \text{deg}^{-2}$
CO	-2.50	52.99	0.31
COC	-2.23	35.84	0.21

Table 3. Most probable values of the five parameter fit.

	CO	COC	CE2 [8]
$\phi_0/\text{deg cm}^{-1}$	-2.67	-2.46	-4.8
$A/\text{K}^{1/2} \text{deg cm}^{-1}$	-0.00512	-0.02385	1.25
$f(x, T - T_2^*)$	0.088	0.423	0.17
$T_1^*/^\circ\text{C}$	53.31	36.39	116.13
$T_2^*/^\circ\text{C}$	53.56	36.44	117.02
$(T_{\text{tr}} - T_2^*)/^\circ\text{C}$	0.01	0.03	0.13

In order to include also the temperature range where coupling exists, a five parameter fit according to equation (3) has been made with the parameters summarized in table 3. The numerical values are very similar for CO and COC, but they differ substantially from the set of parameters obtained by Battle *et al.* [8] for CE2 (in all fits it is assumed that c/b in equation (3) equals unity).

6. Conclusions

These measurements show that in the isotropic phase of CO and COC the pretransitional increase of the optical activity, going according to the Landau-de Gennes description as $(T - T_1^*)^{-1/2}$, is complemented by a divergence of the opposite sign. This latter effect, due to coupling between modes, eventually overrules the former because it has a higher critical temperature. The data show a satisfactory agreement with a simplified form of the relations proposed by Filev [6].

References

- [1] BELYKAOV, V. A., and DIMITRIENKO, V.E., 1985, *Soviet Phys. Usp.*, **28**, 535.
- [2] DE GENNES, P. G., 1969, *Physics Lett. A*, **30**, 454.
- [3] CHENG, J. and MEYER, R. B., 1974, *Phys. Rev. A*, **9**, 2744.
- [4] DOLGANOV, V. K., KRYLOVA, S. P., and FILEV, V. M., 1980, *Zh. eksp. teor. Fiz.*, **78**, 2343 (*Soviet Phys. JETP*, **51**, 1177).
- [5] BENSIMON, D., DOMANY, E., and SHTRIKMAN, S., 1983, *Phys. Rev. A*, **28**, 427.
- [6] FILEV, V. M., 1983, *Pis'ma Zh. eksp. teor. Fiz.*, **37**, 589 (*JETP Lett.*, **37**, 703).
- [7] DEMIKHOV, E. I and DOLGANOV, V. K., 1983, *Pis'ma Zh. eksp. theory. Fiz.*, **38**, 368 (*JETP Lett.*, **38**, 445).
- [8] BATTLE, P. R., MILLER, J. D., and COLLINGS, P. J., 1987, *Phys. Rev. A*, **36**, 369.
- [9] BEEVERS, M. S., ELLIOTT, D. A., and WILLIAMS, G., 1981, *Molec. Crystals liq. Crystals A*, **24**, 635.
- [10] CHARNEY, E., 1979, *The Molecular Basis of Optical Acticity* (Wiley).